

**MOHAMED KHIDER UNIVERSITY OF BISKRA.**

**FACULTY OF EXACT SCIENCES AND NATURAL AND LIFE SCIENCES**

**DEPARTMENT OF BIOLOGY**

**Semester2: THERMODYNAMICS AND CHEMISTRY OF  
MINERAL SOLUTIONS**

**CHAPTER I**

**Part 1**

**Level: 1<sup>st</sup> year LMD**

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## 1. Chemical equilibrium

### 1.1. Acid-base equilibrium

We find three definitions: Arrhenius (1887) and Brønsted-Lowry (1923), as well as the model of Lewis (1923). In solution chemistry, the most suitable theory is that of Brønsted-Lowry.

#### a. Definition of Arrhenius (1887):

An acid: is a chemical substance capable of releasing  $\text{H}^+$  ions (protons) in aqueous solution ( $\text{H}_3\text{O}^+$ : oxonium or hydronium ion).

Example:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$  (HCl,  $\text{CH}_3\text{COOH}$ , ....)

A base: is a chemical substance capable of releasing  $\text{OH}^-$  (hydroxide) ions in aqueous solution

Example:  $\text{BOH} + \text{H}_2\text{O} \rightleftharpoons \text{B}^+ + \text{OH}^-$  (NaOH, KOH, ....)

#### b. Definition from Bronsted and Lowry (1923):

An acid: is a chemical species capable of releasing one or more  $\text{H}^+$  protons; it is a proton donor.

Example:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$  (HCl,  $\text{CH}_3\text{COOH}$ , ....)

A base: is a chemical species capable of capturing one or more  $\text{H}^+$  protons; it is a proton acceptor.

Example:  $\text{A}^- + \text{H}^+ \rightleftharpoons \text{HA}$

#### c. Definition from Lewis (1923):

An acid: is a body that accepts a pair of electrons

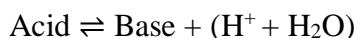
Example:  $\text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \text{H}_3\text{O}^+$  (appearances of a dative bond).

A base: is a body donating a pair of electrons

Example:  $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$  (appearances of a dative bond).

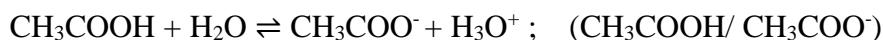
### 2.2. Monoacid and mono-base:

According to Bronsted, an acid is a species capable of releasing an  $\text{H}^+$  proton to give it to another species, and a base is a species capable of capturing a proton coming from another species.



The acid and the base are said: "Conjugates"; they form an acid-base couple noted: Acid/Base).

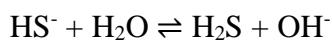
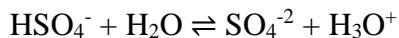
Example:



The acetate ion  $\text{CH}_3\text{COO}^-$  is the conjugate base of acetic acid  $\text{CH}_3\text{COOH}$ .

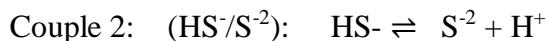
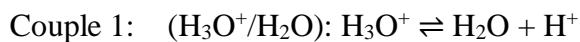
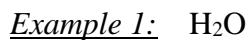
### **2.3. Poly-acids and Poly-bases:**

A polyacid is a species capable of releasing 2 or more protons ( $H^+$ ) to give them to another species, and a base is a species capable of fixing 2 or more protons ( $H^+$ ) from another species.



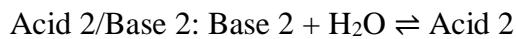
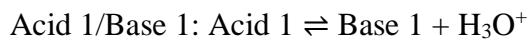
### **2.4. An amphotolytes solution:**

An amphoteric (or amphotolyte) is a chemical species that can behave either as an acid or as a base. The corresponding solutions are called “Amphoteric”.



### **2.5. Acid-base reaction:**

An acid-base reaction is a proton transfer reaction between 2 couples: Acid 1/Base 1 and Acid2/Base2

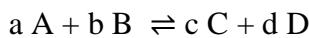


#### **2.5.1. Equilibrium constant: water dissociation, acidity and basicity:**

There are four equilibrium constants:  $K$ ,  $K_e$ ,  $K_a$ ,  $K_b$

a. **Equilibrium constant of a reaction (K):**

The equilibrium constant  $K$  of any acid-base reaction is given by the law of mass action:



$$K = ([C]^c * [D]^d) / ([A]^a * [B]^b)$$

Or  $[A]$ ,  $[B]$ ,  $[C]$  and  $[D]$ : are the concentrations of species A, B, C and D at equilibrium.

b. Water dissociation constant ( $K_e$ ):

The self-protolysis equilibrium of water:  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

$$K_e = \frac{[\text{H}_3\text{O}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad K_e = K \cdot [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$$

$K_e$ : ionic product of water:  $K_e = K \cdot [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$

Calculate the concentration of water  $[\text{H}_2\text{O}]$ :

At  $t=25\text{ C}^\circ$ ,  $K_e = 10^{-14} \Rightarrow pK_e = 14$ .

We have:  $C(\text{H}_2\text{O}) = n(\text{H}_2\text{O})/V(\text{H}_2\text{O})$ , and  $\rho(\text{H}_2\text{O}) = m(\text{H}_2\text{O})/V(\text{H}_2\text{O}) = 1\text{g/ml}$  (or:  $1\text{ g/cm}^3$ )

We take:  $m(\text{H}_2\text{O}) = 1\text{ g} \Rightarrow V(\text{H}_2\text{O}) = 1\text{ ml}$

$n(\text{H}_2\text{O}) = m(\text{H}_2\text{O})/M(\text{H}_2\text{O}) = 1/18 = 0.05555\text{ mol}$  ( $M(\text{H}_2\text{O}) = 2(1) + 16 = 18\text{ g/mol}$ )

$C(\text{H}_2\text{O}) = 0.0555555/1.10^{-3} \Rightarrow C(\text{H}_2\text{O}) = 55.55\text{ mol/l}$ .

c. Acidity constant ( $K_a$ ):

Weak acid:  $\text{AH} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$  (Couple:  $\text{HA}/\text{A}^-$ )

The equilibrium constant:

$$K_a = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{H}_2\text{O}] \cdot [\text{AH}]}$$

The equilibrium constant of dissociation of the acid called “acidity constant  $K_a$ ”:

$$K_a = K \cdot [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{AH}]}$$

Knowing that:  $pK_a = -\log K_a$

Noticed:

Increasing acidity:  $K_a \nearrow \Rightarrow pK_a \searrow$

Increasing basicity:  $K_a \searrow \Rightarrow pK_a \nearrow$

d. Basicity constant ( $K_b$ ):

Weak base:  $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$  (Couple:  $\text{BH}^+/\text{B}$ )

The equilibrium constant:

$$K_b = \frac{[\text{BH}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}] \cdot [\text{B}]}$$

The equilibrium constant of acid dissociation called “acidity constant  $K_b$ ”:

$$K_b = K \cdot [H_2O] = \frac{[BH^+] \cdot [OH^-]}{[B]}$$

### Noticed:

The relationship between  $K_a$  and  $K_b$ :  $K_e = K_a \cdot K_b$

### **2.5.2. pH (Hydrogen potential):**

*a. Definition of pH:* the acidity of an aqueous solution depends on the concentration of  $H_3O^+$  ions.

$$pH = -\log H_3O^+ \quad (p = -\log; H = H_3O^+)$$

### *b. Relationship between pH, $pK_a$ and concentrations:*

Weak acid: Acid (AH) +  $H_2O \rightleftharpoons$  Base (A $^-$ ) +  $H_3O^+$  (Couple: HA/ A $^-$ )

$$K_a = \frac{[H_3O^+] \cdot [Base]}{[Acide]} = \frac{[H_3O^+] \cdot [A^-]}{[AH]}$$

$$K_a \cdot [Acide] = [H_3O^+] \cdot [Base] \Rightarrow [H_3O^+] = K_a \cdot [Acide] / [Base]$$

$$-\log[H_3O^+] = -\log(K_a \cdot [Acide] / [Base]); \quad (pH = -\log H_3O^+; pK_a = -\log K_a).$$

$$pH = pK_a + \log \frac{[Base]}{[Acide]} \quad \text{Relation d'Henderson}$$

### ➤ The pH of the water:

The water auto-protolysis:  $2H_2O \rightleftharpoons H_3O^+ + OH^-$

In pure water the quantities of  $H_3O^+$  and  $OH^-$  ions are equal  $\Rightarrow [H_3O^+] = [OH^-]$

At:  $t=25\text{ C}^\circ$   $K_e = 10^{-14}$ ,  $[H_3O^+] \cdot [OH^-] = K_e = 10^{-14} \Rightarrow [H_3O^+]^2 = K_e = 10^{-14}$

$$\Rightarrow [H_3O^+] = \sqrt{K_e} = \sqrt{10^{-14}} = 10^{-7} \Rightarrow -\log[H_3O^+] = -\log 10^{-7}$$

$$pH(H_2O) = 7$$

### Noticed:

Neutral solution:  $[H_3O^+] = [OH^-] \Rightarrow pH = 7$ .

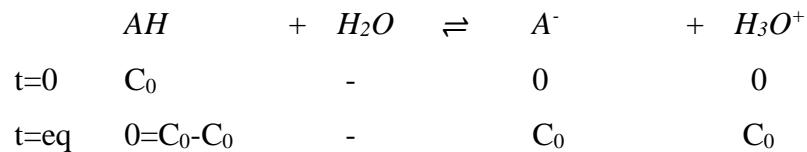
Acid solution:  $[H_3O^+] > [OH^-] \Rightarrow pH < 7$ .

Basic solution:  $[H_3O^+] < [OH^-] \Rightarrow pH > 7$ .

### ➤ The pH of a strong monoacid (SA):

When a Strong Acid (AH) of initial concentration  $C_0$  is dissolved in water, there is total dissociation of the acid:

Couple (HA/A $^-$ ):



In the case of slightly diluted solutions (i.e.:  $C_0 > 3.10^{-7}$  mol/l), the medium is sufficiently acidic so that  $[OH^-]$  resulting from the auto-protolysis of water is negligible compared to  $[H_3O^+]$ .

This means that:  $[H_3O^+] = C_0$ ;  $pH = -\log[H_3O^+] = -\log C_0$ .

$\Rightarrow pH = -\log C_0$ ; ( $[H_3O^+] = C_0$ ).

### Validity of the approximation:

For me to be sure and the acid is strong it is necessary that:  $[H_3O^+] \geq 10[OH^-]$ .

### Demonstration:

$$[H_3O^+] \cdot [H_3O^+] \geq 10 [OH^-] \cdot [H_3O^+]$$

$$[H_3O^+]^2 \geq 10 \text{ Ke} \Rightarrow \text{at } t=25\text{C}^\circ, \text{ Ke} = 10^{-14} \Rightarrow [H_3O^+]^2 \geq 10 \cdot 10^{-14} \Rightarrow [H_3O^+]^2 \geq 10^{-13}$$

$$\Rightarrow [H_3O^+] \geq \sqrt{10^{-13}} = 10^{-6.5} \Rightarrow -\log[H_3O^+] \leq -\log 10^{-6.5} \Rightarrow (\log 10^x = x)$$

$$\Rightarrow pH \leq 6.5$$

### Summary:

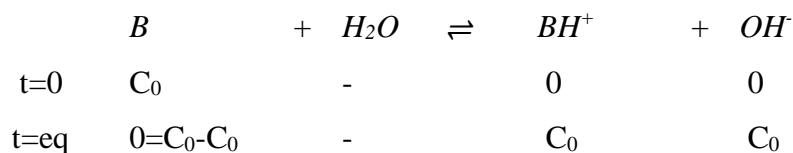
Strong Acid (SA):

$$pH \text{ (SA)} = -\log C_0 \quad ([H_3O^+] = C_0). \quad \text{With} \quad pH \leq 6.5 \quad (\text{at } t=25\text{C}^\circ)$$

### **➤ The pH of a strong mono-base (SB):**

A Strong base (B) with initial concentration  $C_0$ , We have total protonation of the base:

Couple ( $BH^+/B$ ):



In the case of slightly diluted solutions (i.e.:  $C_0 > 3.10^{-7}$  mol/l), the medium is sufficiently basic so that  $[H_3O^+]$  resulting from the auto-protolysis of water is negligible compared to  $[OH^-]$ .

This means that:  $[OH^-] = C_0$ ;

$$[H_3O^+] \cdot [OH^-] = C_0 \cdot [H_3O^+] \Rightarrow Ke = C_0 \cdot [H_3O^+] \Rightarrow [H_3O^+] = Ke / C_0$$

$$-\log[H_3O^+] = -\log(Ke / C_0) \quad (\log A/B = \log A - \log B)$$

$$\Rightarrow pH = -\log Ke + \log C_0, \Rightarrow pH = pKe + \log C_0, \quad [OH^-] = C_0$$

### **Validity of the approximation:**

So that I am sure and the base is strong it is necessary that:  $[\text{OH}^-] \geq 10 [\text{H}_3\text{O}^+]$

## **Demonstration:**

$$[\text{OH}^-] \cdot [\text{H}_3\text{O}^+] \geq 10 \quad [\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{O}^+]$$

$$Ke \geq 10 \ [H_3O^+]^2 \Rightarrow \text{at } t=25C^\circ; Ke = 10^{-14} \Rightarrow 10^{-14} \geq 10 \ [H_3O^+]^2 \Rightarrow 10^{-15} \geq [H_3O^+]^2$$

$$\Rightarrow \sqrt{10^{-15}} = 10^{-7.5} \geq [\text{H}_3\text{O}^+] \Rightarrow -\log 10^{-7.5} \leq -\log [\text{H}_3\text{O}^+] \quad (\log 10^x = x)$$

$$\Rightarrow \text{pH} \geq 7.5$$

## Summary:

### Strong Base (SB):

**pH (SB) = pK<sub>e</sub> + log C<sub>0</sub>,** ([OH<sup>-</sup>] = C<sub>0</sub>). With **pH ≥ 7.5** (at t=25°C)

## ➤ The pH of a weak monoacid (WA):

When a weak acid (HA) of initial concentration  $C_0$  is dissolved in water, there is a partial dissociation of the acid:

Couple (HA/A<sup>-</sup>):  $AH + H_2O \rightleftharpoons A^- + H_3O^+$  (Couple : HA/A<sup>-</sup>)

The water auto-protolysis equilibrium:  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

Four species are present at equilibrium concentration:  $[AH]$ ,  $[A^-]$ ,  $[H_3O^+]$  and  $[OH^-]$

We can write four relationships between these four unknowns:

1. Ionic product:  $K_e = [H_3O^+]. [OH^-]$  .....(1)
2. Couple acidity constant (HA/A<sup>-</sup>):  $K_a = [A^-]. [H_3O^+]/ [AH]$  .....(2)
3. Concentration of the constituent elements of the acid-base couple:  $C_0 = [AH] + [A^-]$  .....(3)
4. Electro-neutrality of the solution:  $[H_3O^+] = [A^-] + [OH^-]$  .....(4)

## **First approximation:**

The medium is acidic:  $[\text{H}_3\text{O}^+] \gg [\text{OH}^-]$ , i.e. the  $[\text{OH}^-]$  is negligible compared to  $[\text{H}_3\text{O}^+]$

The relation (4) becomes:  $[\text{H}_3\text{O}^+] = [\text{A}^-]$  .....(5)

## Second approximation:

The dissociation of the acid is weak, i.e.: the concentration of the conjugated mono-base is negligible compared to that of the acid  $\text{AH}$ , this means that:  $[\text{A}^-] \ll [\text{AH}]$

The relation (3) becomes:  $C_0 = [AH]$  .....(6)

The relation (2) + (5) + (6), we obtain:  $K_a = [H_3O^+]^2 / [AH] \Rightarrow [H_3O^+]^2 = K_a \cdot [AH]$

$$\Rightarrow [H_3O^+] = \sqrt{Ka \cdot [AH]} \Rightarrow -\log[H_3O^+] = -\log(Ka \cdot [AH])^{1/2}; \quad (\log A/B = \log A - \log B)$$

$$\Rightarrow \text{pH} = \frac{1}{2} (-\log K_a - \log [AH]) \Rightarrow \text{pH} = \frac{1}{2} (pK_a - \log [AH]) \Rightarrow \text{pH} = \frac{1}{2} (pK_a - \log C_0),$$

### **Validation Domain:**

The medium is acidic:  $[AH] \geq 10 [A^-]$

### **Demonstration:**

$$[AH] \geq 10 [A^-] \Rightarrow 10^{-1} \geq [A^-]/[AH] \Rightarrow \log 10^{-1} \geq \log[A^-]/[AH] \Rightarrow -1 \geq \log[A^-]/[AH]$$

$$\Rightarrow pK_a - 1 \geq pK_a + \log[A^-]/[AH]$$

According to Henderson relation:  $pH = pK_a + \log ([base]/[acid])$

$$\Rightarrow pK_a - 1 \geq pH \Rightarrow pH \leq pK_a - 1.$$

### **Use of the dissociation coefficient ( $\alpha_a$ ):**

The weak acid approximation relies on the assumption of weak dissociation.

We call:  $(\alpha_a)$ : dissociation coefficient = Number of moles dissociated from AH/Initial number of moles of AH,  $\alpha_a = x/C_0$

### **Material equilibrium:**

|                    |                   |   |        |                      |               |   |               |
|--------------------|-------------------|---|--------|----------------------|---------------|---|---------------|
|                    | $AH$              | + | $H_2O$ | $\rightleftharpoons$ | $A^-$         | + | $H_3O^+$      |
| $t=0$              | $C_0$             |   | -      |                      | 0             |   | 0             |
| $t=eq$             | $C_0 - X$         |   | -      |                      | X             |   | X             |
| $\alpha_a = X/C_0$ | $C_0(1-\alpha_a)$ |   | -      |                      | $C_0\alpha_a$ |   | $C_0\alpha_a$ |

$$Ka = [A^-] \cdot [H_3O^+]/[AH] = C_0\alpha_a \cdot C_0\alpha_a / C_0(1-\alpha_a) = C_0 \alpha_a^2 / (1-\alpha_a) \Rightarrow Ka = C_0 \alpha_a^2 / (1-\alpha_a)$$

• If  $\alpha_a \leq 0.1$  (the dissociation is weak; less than 10%)  $\Rightarrow$  we can neglect the  $\alpha_a$  in front of 1:

$$\text{The relationship becomes: } Ka = C_0 \cdot \alpha_a^2 \Rightarrow \alpha_a = \sqrt{Ka/C_0} \leq 10^{-1} \Rightarrow Ka/C_0 \leq 10^{-2}.$$

### **Note:**

This is Ostwald's law which indicates that dissociation increases with dilution and a much diluted weak electrolyte behaves like a strong electrolyte. This is why the calculation of the pH of acids and bases is applicable for solutions which are not too diluted.

### **Summary:**

Weak acid (WA):

$$pH (WA) = \frac{1}{2} (pK_a - \log C_0) \quad . \quad (t=25C^\circ)$$

With : 1/  $pH \leq pK_a - 1$  ; 2/ If  $\alpha_a \leq 0.1 \Rightarrow Ka/C_0 \leq 10^{-2}$ .

### **➤ The pH of a weak mono-base (WB):**

A weak base (B) with initial concentration  $C_0$ , We have partial protonation of the base:



Four species are present at equilibrium concentration: [B], [BH<sup>+</sup>], [H<sub>3</sub>O<sup>+</sup>] and [OH<sup>-</sup>]

We can write four relationships between these four unknowns:

1. Ionic product:  $Ke = [H_3O^+] \cdot [OH^-] \dots\dots\dots(1)$

2. Couple basicity constant (BH<sup>+</sup>/B):  $Kb = [BH^+] \cdot [OH^-] / [B] \dots\dots\dots(2)$

3. Concentration of the constituent elements of the acid-base couple:  $C_0 = [B] + [BH^+] \dots\dots\dots(3)$

4. Electro-neutrality of the solution:  $[BH^+] + [H_3O^+] = [OH^-] \dots\dots\dots(4)$

### First approximation:

The medium is basic:  $[OH^-] \gg [H_3O^+]$ , i.e. the  $[H_3O^+]$  is negligible compared to  $[OH^-]$

The relation (4) becomes:  $[BH^+] = [OH^-] \dots\dots\dots(5)$

### Second approximation:

The protonation of the base is weak, i.e.: the concentration of the conjugated monoacid is negligible compared to that of base B, this means that:  $[BH^+] \ll [B]$ .

The relation (3) becomes:  $C_0 = [B] \dots\dots\dots(6)$

$$Kb = [BH^+] \cdot [OH^-] / [B] \dots\dots\dots(2) \quad (Ka \cdot Kb = Ke; Ke = [H_3O^+] \cdot [OH^-])$$

$$\Rightarrow Ke/Ka = [BH^+] Ke / [B] [H_3O^+] \Rightarrow Ke \cdot [B] \cdot [H_3O^+] = Ka \cdot [BH^+] \cdot Ke$$

$$\Rightarrow Ka = [B] \cdot [H_3O^+] / [BH^+] \dots\dots\dots(7)$$

$$(7) + (5) + (6), we obtained: Ka = C_0 \cdot [H_3O^+] / [OH^-] \Rightarrow Ka = C_0 \cdot [H_3O^+]^2 / Ke$$

$$\Rightarrow [H_3O^+]^2 = (Ka Ke / C_0) \Rightarrow [H_3O^+] = \sqrt{(Ka Ke / C_0)} \Rightarrow -\log[H_3O^+] = -\log(Ke Ka / C_0)^{1/2};$$

$$(\log A/B = \log A - \log B, \log A \cdot B = \log A + \log B)$$

$$\Rightarrow pH = \frac{1}{2} (-\log Ka - \log Ka + \log C_0) \Rightarrow pH = \frac{1}{2} (pKe + pKa + \log C_0)$$

### Validation Domain:

The medium is basic:  $[B] \geq 10 [BH^+]$

### Demonstration:

$$[B] \geq 10 [BH^+] \Rightarrow 10^{-1} \geq [BH^+]/[B] \Rightarrow [B]/[BH^+] \geq 10 \Rightarrow \log[B]/[BH^+] \geq \log 10$$

$$\Rightarrow pKa + \log[B]/[BH^+] \geq pKa + 1 \quad (\text{Henderson relation: } pH = pKa + \log ([\text{base}]/[\text{acid}]))$$

$$\Rightarrow pH \geq pKa + 1.$$

### Use of the dissociation coefficient ( $\alpha_b$ ):

The weak basis approximation relies on the assumption of weak protonation

We call: ( $\alpha_b$ ): dissociation coefficient = Number of moles dissociated from [B] / Initial number of moles of [B],  $\alpha_b = x/C_0$ .

### Material equilibrium:

|                    |                   |     |        |                      |               |     |               |
|--------------------|-------------------|-----|--------|----------------------|---------------|-----|---------------|
|                    | $B$               | $+$ | $H_2O$ | $\rightleftharpoons$ | $BH^+$        | $+$ | $OH^-$        |
| $t=0$              | $C_0$             |     | -      |                      | 0             |     | 0             |
| $t=eq$             | $C_0 - X$         |     | -      |                      | $X$           |     | $X$           |
| $\alpha_b = X/C_0$ | $C_0(1-\alpha_b)$ |     | -      |                      | $C_0\alpha_b$ |     | $C_0\alpha_b$ |

$$K_b = [BH^+] \cdot [OH^-] / [B] \quad (K_a \cdot K_b = K_e; \quad K_e = [H_3O^+] \cdot [OH^-])$$

$$\Rightarrow K_e / K_a = [BH^+] K_e / [B] [H_3O^+] \Rightarrow K_e \cdot [B] \cdot [H_3O^+] = K_a \cdot [BH^+] \cdot K_e$$

$$\Rightarrow K_a = [B] \cdot [H_3O^+] / [BH^+] \Rightarrow K_a = K_e \cdot [B] / [BH^+] [OH^-] \Rightarrow K_a = K_e C_0(1-\alpha_b) / C_0\alpha_b \cdot C_0 \alpha_b$$

$$\Rightarrow K_a = K_e (1-\alpha_b) / C_0 \alpha_b^2$$

- If  $\alpha_b \leq 0.1$  (the protonation is weak; less than 10%)  $\Rightarrow$  we can neglect the  $\alpha_b$  in front of 1:

The relationship becomes:  $K_a = K_e / C_0 \alpha_b^2 \Rightarrow \alpha_b = \sqrt{(K_e / K_a C_0)} \leq 10^{-1} \Rightarrow K_e / K_a C_0 \leq 10^{-2}$ .

### Summary:

Weak base (WB):

$$pH(WB) = \frac{1}{2} (pK_e + pK_a + \log C_0) \quad . \quad (t=25C^\circ)$$

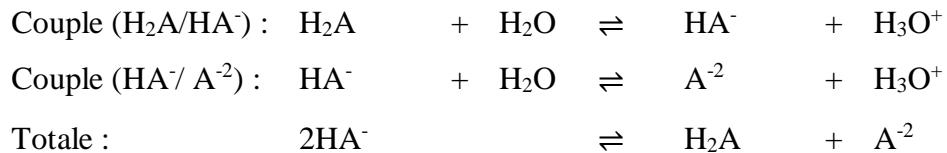
With : 1/  $pH \geq pK_a + 1$ ; 2/ If  $\alpha_b \leq 0.1 \Rightarrow K_e / K_a C_0 \leq 10^{-2}$ .

### ➤ The pH of an amphoteric solution:

Consider the solution of a NaHA salt (Example: Na HCO<sub>3</sub>) of concentration C.

The total dissociation of salt in water is written as: NaHA<sub>(solid)</sub>  $\rightarrow$  Na<sup>+</sup> + HA<sup>-</sup>

HA<sup>-</sup> is an amphotolyte since it is the acid pair: HA<sup>-</sup>/A<sup>-2</sup> and the base of H<sub>2</sub>A/HA<sup>-</sup>



The balance of this overall reaction indicates that: [H<sub>2</sub>A] = [A<sup>-2</sup>]

Ka<sub>1</sub>: acidity constant: H<sub>2</sub>A/HA<sup>-</sup>  $\Rightarrow$  Ka<sub>1</sub> = [HA<sup>-</sup>] · [H<sub>3</sub>O<sup>+</sup>] / [H<sub>2</sub>A]

Ka<sub>2</sub>: acidity constant: HA<sup>-</sup>/A<sup>-2</sup>  $\Rightarrow$  Ka<sub>2</sub> = [A<sup>-2</sup>] · [H<sub>3</sub>O<sup>+</sup>] / [HA<sup>-</sup>]

$$K_{a1} \cdot K_{a2} = ([HA^-] \cdot [H_3O^+] / [H_2A]) \cdot ([A^{-2}] \cdot [H_3O^+] / [HA^-]) = [H_3O^+]^2 \cdot ([A^{-2}] / [H_2A])$$

$$[H_2A] = [A^{-2}]$$

$Ka_1 \cdot Ka_2 = [H_3O^+]^2 \Rightarrow pH = \frac{1}{2} (pKa_1 + pKa_2)$  (We note that pH is independent of concentration (C)).

**Noticed:**

An amphotelyte is a substance that contains a negative charge and hydrogen (regardless of the number of negative charges or hydrogen atoms).